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Research Division
NATIONAL RESEARCH CORPORATION
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Cambridge 42, Massachusetts

Nonr-3608(00)

Semi-Annual Technical Summary Report

July 1, 1963 - December 31, 1963

THERMODYNAMIC PROPERTIES OF BIMETALLIC COMPOUNDS (U)

Mr. Ludwig Fasolino
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DOWNGRADED AT 3 YEAR INTERVALS
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Advanced Research Projects Agency
The Pentagon, Room 3D-159
Washington 25, D. C.
Attn: Advanced Propellant Chemistry Office

January 31

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INTRODUCTION

Of interest to the propellant field are several chemical compounds whose thermodynamic properties are required for reliable propulsion calculations.

This laboratory is engaged in the determination of the heats of formation of some of these compounds by precision calorimetric methods. The method most frequently used is that of solution calorimetry at various temperatures. When not applicable, methods such as oxygen and fluorine combustion have been employed.

The calorimetric measurements are made adiabatically in closed bomb (for gas evolving reactions) and in glass dewar (no gas evolution) reaction vessels. Temperature is measured as an amplified thermistor output enabling high sensitivity.

SUMMARY

The heats of formation of the aluminum hydrides designated Olane-58 and Dowane-1451 were determined by measuring the heats of solution of these compounds and aluminum in 6N HCl at 75°C. Correcting the data to 25°C yielded the following results:

	ΔHf_{298}, kcal mole^{-1}
Olane-58	-4.6 ± 1.6
Dowane-1451	-2.5 ± 3.7

The heat of formation of the Reaction Motors material, Li_3AlH_6, was determined by measuring the heats of solution of lithium, aluminum, and Li_3AlH_6 in 4N HCl at 25°C:

$$\Delta Hf_{298}\ Li_3AlH_6 = -79.39 \pm 3.45 \text{ kcal mole}^{-1}$$

A fluorine combustion calorimeter was assembled, calibrated, and utilized in preliminary combustion studies of the Al-B system.

A silvered, dewar-type reaction vessel was assembled in which solution studies of B_2O_3 (amorph.), B_2O_3 (c), H_3BO_3, BCl_3, and BF_3 are to be made.

I Heat of Formation of the Aluminum Hydrides, Olane-58 and Dowane-1451

The heats of formation of the aluminum hydrides, Olane-58 and Dowane-1451, have been determined by measuring the heats of solution of the hydrides, and aluminum in 6.0N HCl at 75°C. This study demonstrated the successful employment of an acid solution calorimeter operating adiabatically at this elevated temperature.

The heats of solution corrected to 25°C are as follows:

	ΔH_{298}, kcal mole^{-1}
Olane-58	-125.03 ± 1.25
Dowane-1451	-127.11 ± 3.26
Aluminum	-129.56 ± 2.00
Aluminum[(a)]	-129.64 ± 0.39

From this data, the heats of formation of Olane-58 and Dowane-1451 were calculated to be:

	ΔHf_{298}, kcal mole^{-1}
Olane-58	- 4.6 ± 1.6
Dowane-1451	- 2.5 ± 3.7

The details of this work are covered in the National Research Corporation Special Report, "Heat of Formation of Aluminum Hydride", August 1, 1963, (Nonr-3608(00)).

(a) Measurements made in 4N HCl at 25°C and corrected to 6N HCl.

II Heat of Formation of the Reaction Motors Material, Li_3AlH_6

The heat of formation of a material, Li_3AlH_6, (synthesized at Reaction Motors) has been determined in this laboratory by measuring the heats of reaction of aluminum, lithium, and Li_3AlH_6 in 4N HCl at 25°C in a closed bomb.

The heats of solution were found to be:

	ΔH_{298}, kcal mole^{-1}
Aluminum	-128.14 ± 0.39
Lithium	- 67.05 ± 0.53
Li_3AlH_6	-249.90 ± 1.47

From this data, the heat of formation of Li_3AlH_6 was calculated to be:

$$\Delta Hf_{298} (Li_3AlH_6) = -79.4 \pm 3.4 \text{ kcal mole}^{-1}$$

The details of this work are covered in the National Research Corporation Special Report, "Heat of Formation of Li_3AlH_6", October 9, 1963 (Nonr-3608(00)).

III Fluorine Combustion Calorimeter

A fluorine combustion calorimeter was assembled for those materials which could not feasibly be studied by acid solution methods. Aluminum-boron is such a system.

Techniques were developed which permitted charging of the bomb at various fluorine pressures, and involved the mani-

pulation of liquid and/or gaseous fluorine in a tight manifold. As part of this study to determine the heat of formation of AlB_2 by fluorine combustion, it was necessary to establish a satisfactory furnace configuration within the bomb which would withstand the energetic combustion. The configuration adopted utilized CaF_2-coated alumina discs and crucibles, and was found to withstand the thermal shock without shattering.

The material designated as AlB_2 was found to be AlB_{12} plus aluminum. The aluminum was removed and the AlB_{12} was used in these initial combustion studies, although the heat of formation of AlB_{12} was not being sought. Combustions were carried out at various pressures of fluorine with boron and AlB_{12} in the form of loose powders and again as pellets containing various portions of teflon powder. The teflon powder enabled the material to be pelletized and aided ignition.

The conditions which yielded nearly 100% combustion required a fluorine pressure of 125 psig and a material to teflon ratio of 1 to 4.

Although no quantitative thermochemical data were generated on the AlB_{12} system, the fluorine combustion method of calorimetric study was developed to a point where quantitative studies are possible.

IV Solution Calorimeter

A silvered, dewar-type reaction vessel was assembled in which the heats of solution of B_2O_3, (amorphous and crystalline), H_3BO_3, BCl_3, and BF_3 will be measured. From these measurements, the heats of formation of B_2O_3, (amorphous and crystalline), BCl_3, and BF_3 will be calculated. Initial preliminary runs show that an adiabatic approach will improve the accuracy of this measurement. A technique has been developed to enable this to be done with our immersed dewar, in which the relatively fast reaction takes place. Simulation runs are in progress and are to be followed by electrical calibrations.

A drying vacuum furnace has been assembled to dry the oxides and boric acid, and also to prepare the amorphous boron oxide.

The first measurements will be the heat of hydrolysis of crystalline B_2O_3.

V Presentations

During this period presentations of the work generated in this program were given at the Annual Calorimetry Conference, October 16-18, Bartlesville, Oklahoma, and at the JANAF Thermochemical Panel Meeting, November 5-7, New York City.

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